

A nanoscale soft-ionization membrane: A novel ionizer for ion mobility spectrometers for space applications

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ABSTRACT

The Jet Propulsion Laboratory (JPL) has developed a novel nanometer-thick Soft Ionization Membrane (SIM) which is capable of ionizing nearly 100% of the gases that pass through it. Both sides of the membrane are coated with a metallic conducting film. A modest potential of less than 10 Volts across the membrane produces an electric field in excess of 10^7 V/cm over a region that is smaller than the mean free path of gas molecules which ionizes the neutral molecules that passing through. Because the region of high electric field is smaller than the mean free path of gas molecules, there are virtually no high energy collisions and the system does not suffer from the fatal problem of avalanche breakdown. The soft ionization mechanism does not fracture the medium or cause any secondary ionization. Thus, a truly new ionization technique is enabled by a simple nanoscale micromachined device. The SIM is tiny, rugged and well suited for a wide variety of applications ranging from space micropropulsion systems to miniature analytical separation devices. In this paper we focus our attention on ion mobility spectrometers (IMSs) as a potential candidate to be incorporated with SIM.

Keywords: soft ionization, ion mobility spectrometers, Mars

1. INTRODUCTION

Miniature mass spectrometry is a powerful *in-situ* tool for identifying a wide variety of chemical compounds. For applications that cover many disciplines such as planetary exploration, residual gas analysis, and environmental applications, there is a need for an *in-situ* analytical separation device or chemical sensor which is rugged, light weight, low power, small, fast, and requires minute quantities of sample for analysis. These requirements are also applicable for a mass or chemical sensor for use on the battlefield (sensing explosives and chemical warfare agents), and for the detection of certain organics in the medical sciences.

The starting point for a mass spectrometric analysis is the formation of gaseous analyte ions, and the scope and utility of a mass spectrometric method is dictated by the ionization process.¹ Ion sources are classified as being hard ionization or soft ionization sources. Hard ionization sources, such as the most commonly used electron-impact (EI) sources, have three major shortcomings: a) *Fragmentation of target molecules.* These type of sources impart sufficient energy to target molecules so that they are left in a highly excited energy state. Relaxation then involves rupture of bonds resulting in fragment ions that have mass-to-charge ratios less than that of the molecular ion. Soft ionization sources, however, cause little or no fragmentation. Consequently, the resulting mass spectrum often consists of the molecular peak and only very few, if any other, peaks. Soft ionization methods have a distinct advantage over hard ionization techniques especially when a mixture of chemicals is to be analyzed. The complexity of break-up patterns of the chemicals puts extremely severe constraints on the unique identification of the parent molecules. b) *Low sensitivity.* Electron-impact induced ionization is not very efficient, and only about one molecule in a million undergoes the primary reaction



where M is the target molecule, is e^- electron, and M^{*+} is its molecular ion. The inefficiency of the ion production (i.e., number of target ions created by EI is low) results in a decreased level of the detection sensitivity of the mass spectrometer. c) *High vacuum requirement.* All presently used conventional mass spectrometers operate at a pressure of 10^{-6} - 10^{-9} Torr.² This pressure regime requires powerful pumps which greatly increases the size, weight and mechanical complexity of the mass analyzer.^{3,4}

Development of a state-of-the-art, low-power, low-mass and robust in-situ instrument for detection of variety of species without the problems associated with the conventional in-situ mass analyzers such as the fragmentation problem, low-sensitivity and high-vacuum requirement, is necessary for many space and terrestrial applications.

With the above requirements and applications in mind, we have designed a novel nanometer-thick Soft Ionization Membrane (SIM) to be incorporated into a wide variety of mass spectrometers. The SIM is capable of ionizing nearly 100% of the molecules that pass through it. Both sides of the membrane are coated with a metallic conducting film. A modest potential of less than 10 Volts across the membrane produces an electric field in excess of 10^7 V/cm over a region that is smaller than the mean free path of gas molecules and ionizes the neutral molecules that pass through the holes. Because the region of high electric field is smaller than the mean free path of gas molecules, there are virtually no high energy collisions and the system does not suffer from the fatal problem of avalanche breakdown. The soft ionization mechanism does not fracture the target molecules or cause any secondary ionization. Thus, a truly new ionization technique is enabled by a simple nanoscale micromachined device. The SIM is tiny, rugged and well suited for ion mobility spectrometers (IMSS) as a front-end ionization device.

2. DETAILS OF THE DESIGN AND FABRICATION OF SIM

Nanoscale electromechanical systems (NEMS) techniques were used to manufacture a membrane used to supply singly charged un-fractured ions for mass spectrometry. The innovative nanostructure, developed at the Jet Propulsion Laboratory (JPL), is a major advance over micromachined volcano field ionization devices and filaments or other energy-intensive devices, achieving nearly 100% ionization of gases and vapors without appreciable fracture.^{5,6} This compares with 0.01-10% ionization using other techniques. The high degree of ionization leads to a large increase in sensitivity over systems using other techniques. The SIM produces only positively charged ions, most of which are singly charged. Other techniques produced positive and negative ions with multiple charge states, which can reduce sensitivity and complicate data interpretation.

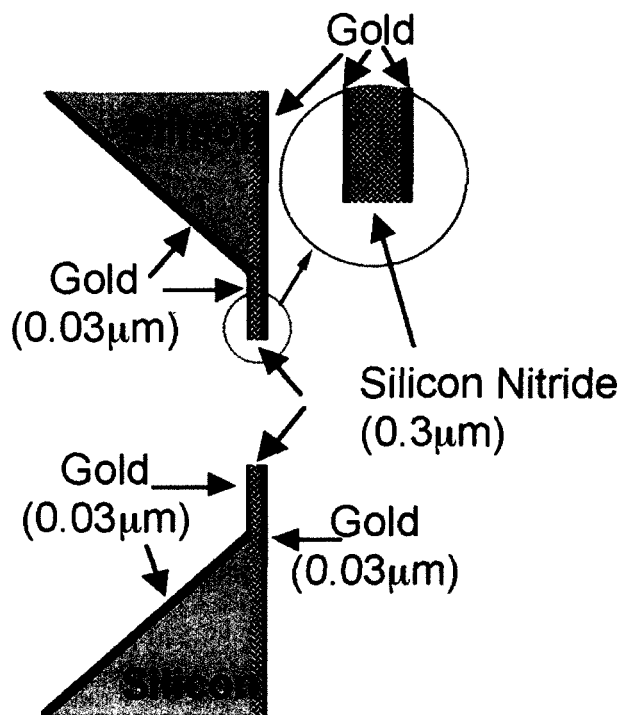


Figure 1: Single Pore Element of the Soft Ionizing Membrane (SIM)

The SIM is a composite structure consisting of electrodes, insulators, and support structure. Figure 1 illustrates the concept, which is realized by micro-machining very small holes through a thin (sub-micron) membrane that has metal electrodes on each side of it. Figure 2 shows the resolution of the manufacturing methods, in an e-beam

micrograph of a chemically assisted FIB eroded (maskless) hole (~2 μm dia.) through a 300 nm Nitride membrane (dark segment) and gold coatings (top and bottom). Ions are created in the submicron structures in the membrane pores by

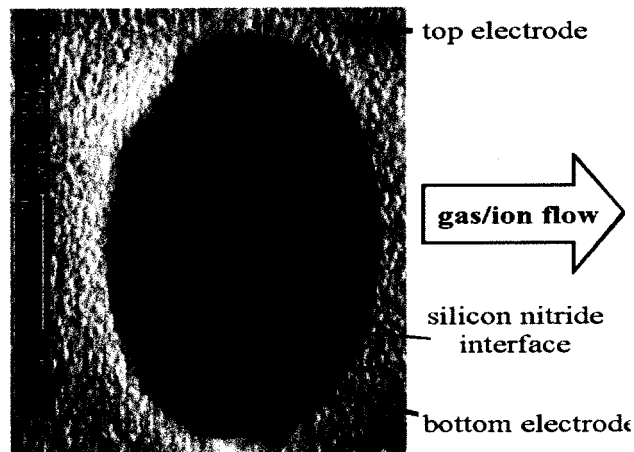


Figure 2: Photomicrograph of Pore

extreme electric fields for small dc voltage impressed between the electrodes. For example, a 3-volt potential across a 0.3-micron gap produces 10,000,000 V/m. The electric field model (Figure 3) demonstrates the maximum field at the rim of a pore and the moderate attenuation of the field at the center of the pore (~20%). Ten or more volts applied across the membrane can create extreme voltage gradients which greatly exceed that necessary to strip electrons from gas molecules and thus ionize them. The field, even with 20% attenuation at the center of the pore (20% radius represents only 4% of pore area), is more than necessary to singly ionize 100% of the medium passing through it. Because the flight-path of gas molecules between collisions is greater than the electrode separation (beneath the Paschen curve) few secondary collisions occur that can split larger molecules and only singly charged ions are produced.

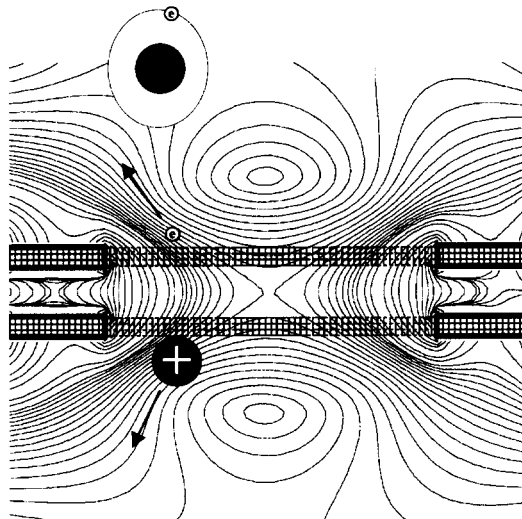


Figure 3: Electric Field Model of Ionization Membrane

The other crucial property of the SIM is its softness. Molecules are ionized by a high electric field that extends over only a short distance (~0.3 μm). The resulting electron and ion quickly pass through the high field region without gaining much energy. Therefore, the ions are not fragmented by subsequent collisions. This greatly increases

sensitivity. The large flux of ions and lack of fragmentation allows the system to be used at much higher pressure than conventional mass spectrometers (1 Torr versus 10^{-3} - 10^{-6} Torr).

Ionization that does not fragment or multiply-ionize the sampled species is a boon to many ion discrimination instruments. Further, the efficiency of the ion stream is expected to provide the detection of vapor-phase compounds at least at the low parts-per-billion level, performance that exceeds many detection capabilities by up to four orders of magnitude.

Figure 4a presents a demonstration of the non-fragmenting attribute of soft ionization in the mass spectrometry for the Sarin analog - Dimethyl Methane Phosphate (DMMP) in a dirty air environment. The SIM ionization leaves the DMMP largely intact and singly charged (124.08 amu) and readily identifiable.

By comparison, the same sample analyzed using plasma ionization (hard ionization) in a bending magnet mass spectrometer (Figure 4b) completely fractures the DMMP and charges components both negatively and positively. It is not possible to identify DMMP in these results.

Field Ionizer Rotating Field Mass Spectrometer

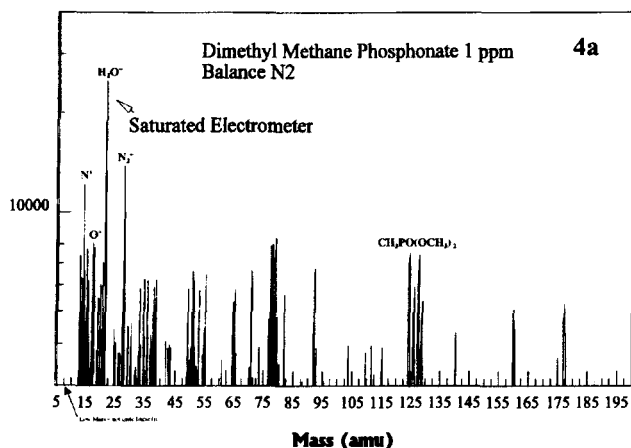


Figure 4a: Soft -ionization mass spectrum of Dimethyl Methane Phosphate (DMMP).Methane.

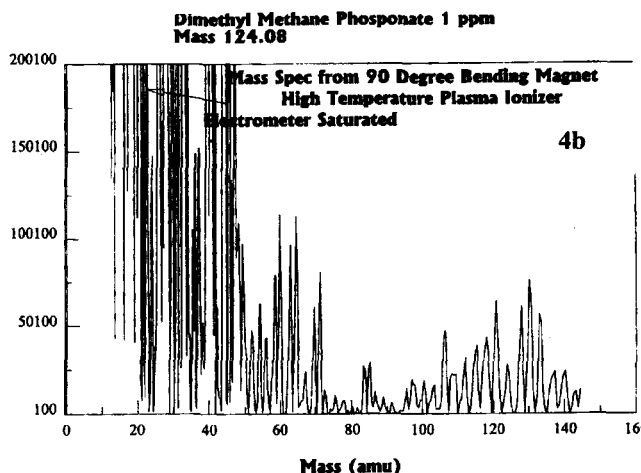


Figure 4b: Hard -ionization mass spectrum of Dimethyl Phosphate (DMMP).

The National Institute of Standards and Technology (NIST) has run pure DMMP at high vacuum in their mass spectrometer using electron beam ionization. The results (Figure 4c) show that little of the sample remains unfractured at 124 amu. The fragments have lower mass and can be confused with other species in a typical dirty environment. This comparison clearly shows the advantage of the soft ionization membrane. This data indicates that DMMP will be readily detectable at ppb sublethal levels using the SIM.

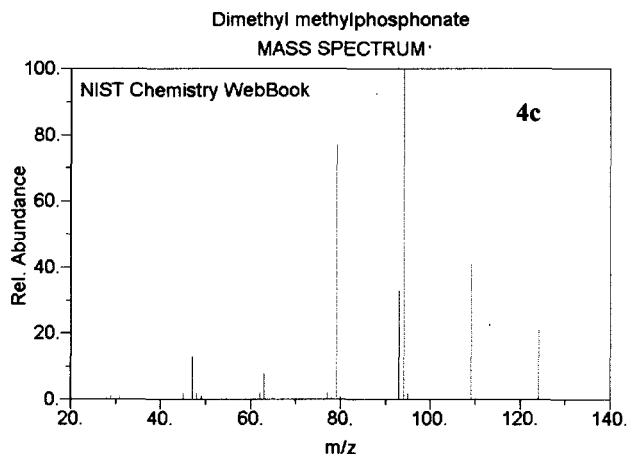


Figure 4c: Hard -ionization mass spectrum of Dimethyl Phosphate (DMMP) using EI ionization.

3. SOFT IONIZATION MEMBRANE/ION MOBILITY SPECTROMETER

The SIM can easily be incorporated in various mass spectrometers as a generic front-end ionizer. For space applications such as future Mars missions, the IMS detection technique is ideally suited to be incorporated with the SIM because IMS provides benefits which cannot be matched readily or reliably by other mass spectroscopy techniques. In particular, IMS is simple, very rapid in comparison with chromatographic separations, highly selective, and highly sensitive (parts-per-billion or better) to a wide range of compounds.⁷ Furthermore, when incorporated with SIM, the IMS technique does not require high vacuum to operate under Martian atmospheric pressure (~5 Torr). Despite these advantages IMS has seen very little use as an analytical separation device, perhaps due to the perception that it is a low-resolution technique, where the *resolution* is defined as the efficiency of the separation and the selectivity of the separation. However, recently the JPL group has utilized a new high-resolution IMS device incorporating an electrospray ionization source. The results have demonstrated that the IMS has an ability to separate even isomers, i.e., chemical compounds that have same molecular weight but different structure, such as leucine and isoleucine.⁸

The operating principles of IMS is simple.⁹ The reactant and product ions with specific polarity are caused to drift in the axial direction by imposing an electric field by means of a bias voltage. Either positive or negative ions can be detected, depending on the polarity of this field. In order to determine the drift velocity, the ions are introduced into the drift region in a pulsatile, i.e. time-dependent manner. This is accomplished by use of a shutter grid comprised of an array of parallel wires, the function of which is to establish a localized repeller field (**E**). The wires are biased such as to provide a potential difference between alternate wire positions. Proper spacing between the wires permits very precise control of the ion flow in response to a relatively small control-voltage change across the shutter wires. When the shutter is closed, the ion flow is blocked, and when the potential is removed, the ions can drift freely toward the collector, driven by the main electric field. Following the admittance of each batch of sample, the relative ion current signatures will yield full information on the type of chemical compounds, as well as the concentrations.

Within the drift region, the ions will undergo spatial separation based on size, mass, and shape. For a given electric field **E**, the ion drift velocity is directly proportional to the specific mobility. Smaller ions travel faster, and thus have higher mobility than the larger ions that arrive later. By measuring the ion drift times for a particular set of conditions, one is then able to construct ion mobility tables that can be used for identification of target ion species. In operation, ions will be introduced into the mass analyzer via a series of pulses (repeated every 20 to 40 ms). A high-gain electrometer will detect the resulting low-noise signal, which is typically at the picoampere (10^{-12} A) level. A microprocessor is to handle data acquisition, processing, communication, and display, as well as control and monitoring of temperature and timing.

3.1 Space Application: Mars

The scientific interest in Mars is rooted in the existence of its atmosphere, without which the possibility of life is remote. The approximate composition of the Martian surface atmosphere, shown in Table 1. Owen et al. raised many scientific questions central to the understanding of Martian atmospheric chemistry and history.¹⁰ A markedly non-equilibrium mixture, it contains both an oxidant (oxygen) and a reducing agent (carbon monoxide). Since both are formed by the well-characterized photochemical decomposition of CO₂, the mixing ratio of CO should exceed that of O₂ by a factor of two.¹¹ In fact, the reverse is true, i.e., there is an apparent deficit of carbon monoxide of almost 75%. No mechanism for formation or loss of either O₂ or CO in quantity has been suggested. In fact, CO is believed to be especially long-lived on Mars.¹² Whether O₂ is in excess or CO is in deficit is unknown, but it is possible that the regolith, by either physical or biological means, is responsible for the discrepancy.¹³

Component	Carbon Dioxide	Nitrogen	Argon	Oxygen	Carbon Monoxide	Water Vapor	Neon	Krypton	Xenon	Ozone
Formula	CO ₂	N ₂	Ar	O ₂	CO	H ₂ O(v)	Ne	Kr	Xe	O ₃
units	% (v)	% (v)	% (v)	% (v)	% (v)	% (v)	ppm (v)	ppm (v)	ppm (v)	ppm (v)
	95.32	2.7	1.6	0.13	0.07	0.03	2.5	0.3	0.08	0.03

The proposed miniature Soft Ionization Membrane/Ion Mobility Spectrometer (SIM/IMS) would enable a quantitative measurement of CO in the presence of massive quantities of CO₂ that is not fragmented. It would be able to characterize the mystery of the CO/O₂ imbalance, a question that may be critical for understanding how the atmosphere

and regolith interact with solar radiation. The summary of characteristics of the proposed high-resolution SIM/IMS instrument is given in Table 2.

Organic analyses of the surface and atmosphere will be of pivotal importance in forthcoming explorations of Mars. The search for both biotic and abiotic organic molecules will be an important part of any Mars missions now envisioned by NASA and the European Space Agency during the next few years. Strategies are being developed to pursue exobiological objectives for Mars, such as determining the abundance and distribution of the biogenic elements and organic compounds, seeking evidence of ancient biota on Mars, and determining whether indigenous organisms exist anywhere on the planet. State-of-the-art *in situ* detection techniques possessing very high sensitivity will play a major role in these endeavors. We are confident that one of the main components of future scientific payloads to Mars (and either of the above bodies)

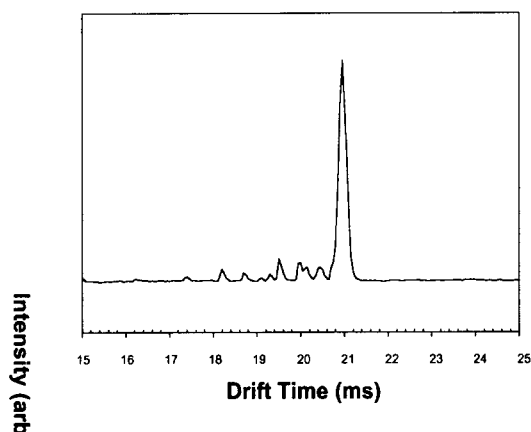


Fig. 5 An ion mobility spectra of Lysine (large peak). The concentration of lysine to solvent was 20 parts-per-billion.

Table 2. Summary of Characteristics of the Proposed High-Resolution SIM/IMS Instrument.

- high sensitivity (parts-per-billion) (see Fig. 5).
- a molecular range up to several million amu with a linear response range of more than 4 orders of magnitude and reproducibility better than 3% (see, ref. 8)
- No fragmentation of fragile biomolecules.
- rugged, simple, and no moving parts.
- no high vacuum or differential pumping required for operation.

will be a chemical analyzer capable of identifying possible organic species. Gas Chromatography/Mass spectrometry (GC/MS) is perhaps the most prominent of techniques presently available for the analysis of organic compounds from a landed spacecraft. In fact, a GC/MS was successfully utilized on the Viking Mars lander. Another GC/MS is presently among the suite of instruments within the Huygens probe that has been launched aboard Cassini and is intended for the detection of molecules in the atmosphere of Titan. However, the present generation of mass spectrometers, being flown on the Galileo and Cassini spacecraft, weigh about 13 kg and consume about 30 Watts of power. Because of limited spacecraft accommodations, scientific instruments must be very low mass (<2 kg) and robust, with minimal power requirements (<10 Watts).

Instruments like this one (i.e. SIM/IMS) could be used on Mars to search for trace organic compounds such as amino acids indicative of life.⁸

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